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ORIGINAL ARTICLE

Mesoporous carbon-coated $Li_4Ti_5O_{12}$ spheres for fast Li^+ ion insertion/deinsertion in lithium battery anodes

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Abstract We report on synthesis and electrochemical properties of a family of carbon-coated, mesoporous lithium titanate nanostructures (C@$Li_4Ti_5O_{12}$). Synthesized using a scalable solvothermal approach employing low-cost petroleum pitch as the carbon source, the nanostructured C@$Li_4Ti_5O_{12}$ materials manifest exceptional capacity to reversibly intercalate/de-intercalate lithium at both low and high charge rates. The combination of fast electrolyte and ion transport made possible in the inherently zero-strain material, $Li_4Ti_5O_{12}$, is thought to be responsible for our observations.

Keywords C@$Li_4Ti_5O_{12}$ · Pitch · Electrochemical study · Lithium battery anode

Introduction

Among the various existing battery technologies, lithium ion batteries (LIBs) have found widespread use in today's electronics and telecommunications sectors. There are three generally accepted reasons for the growing acceptance of LIBs: their high energy density, longer shelf life relative to other secondary battery technologies and broad operating temperature range. In addition, LIBs are space friendly and are widely viewed as the ultimate choice for HEV and PHEV applications (Armand and Tarascon 2008). Despite the remarkable growth and widespread acceptance of LIB technology, the exploitation of LIBs for high power applications has been limited by issues related to safety, capacity fade over many charge/discharge cycles, and slow kinetics of lithium insertion/de-insertion processes in the electrode materials. Accordingly, demand for novel electrode materials capable of rapidly and reversibly intercalating lithium has grown considerably.

In general, capacity fade in LIBs can be attributed to the variation in lattice dimensions of the electrode material as it undergoes repeated charge–discharge reactions (Ohzuku et al. 1995). Materials undergoing electrochemical topotactic transformation associated with the insertion or extraction of Li^+ ions are consequently preferred for potential lithium battery applications (Ohzuku et al. 1995). The cubic spinel $Li_4Ti_5O_{12}$ is one such material which manifests almost zero strain and negligible changes in its crystal lattice structure upon repeated lithium insertion and extraction (Cheng et al. 2010; Park et al. 2008; Prakash et al. 2010). $Li_4Ti_5O_{12}$, is capable of accommodating three Li^+ ions per formula unit at $\sim$1.5 V during charging, and has a theoretical capacity of 175 mAh/g (Ohzuku et al. 1995; Cheng et al. 2010; Park et al. 2008). Though almost half the theoretical capacity of currently used LiC_6 (360 mAh/g), and notwithstanding its high intercalation voltage (Wang et al. 2009; Colbow et al. 1989; Amatucci et al. 2001), $Li_4Ti_5O_{12}$ is attracting considerable attention as the candidate of choice for the LIB anode in high power applications because of its safety and structural stability (Amine et al. 1997, 1998, 2002). In addition, it has been shown that when $Li_4Ti_5O_{12}$ is coupled with high voltage cathode materials

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such as $LiMn_2O_4$ (Pasquier et al. 2009) and $LiNi_{0.5}Mn_{1.5}O_4$ (Wu et al. 2009), the latter limitation is remedied.

Herein we report the synthesis of carbon-coated $Li_4Ti_5O_{12}$ via an in situ carbonization scheme, employing low-cost petroleum-based pitch as the carbon source. We show that the product of this synthesis, C@$Li_4Ti_5O_{12}$, exhibits markedly improved capacity retention, particularly at high rates, when compared to pristine $Li_4Ti_5O_{12}$.

Experimental

Mesoporous TiO_2 with high surface area was synthesized using a modified urea-assisted hydrothermal method at 95°C, as reported previously (Guo et al. 2003; Jung et al. 2009). In a typical synthesis, urea (1 M) and ammonium sulfate (0.01 M) were added to a solution of $TiCl_4$ (0.6 M) in a 1:1 water–ethanol mixture. The contents were transferred to a Teflon-lined autoclave and heated at 95°C for 5 h. The resultant TiO_2 particles were washed, dried and suspended in *N*-methyl-2-pyrrolidone solvent. The suspension was heated at 125°C with stirring until the solvent began to evaporate. A calculated amount of pitch was added to the suspension along with a stoichiometric quantity of lithium carbonate. The suspension was subsequently stirred until complete evaporation of the solvent, and the resultant brown-colored precursor calcined under an Argon atmosphere at 900°C for 20 h. Pristine $Li_4Ti_5O_{12}$ without carbon coating was synthesized using a similar procedure.

Characterization of the samples

Transmission electron microscopy (TEM, Tecnai, T12, 120 kV), powder X-ray diffraction (Scintag X-ray diffractometer with Cu Kα radiation), thermo gravimetric analysis (under air, Thermo Scientific TA Instrument (Nicolet iS10) operated at a heating rate of 20°C min^{-1}), nitrogen adsorption/desorption measurements (Micromeritics ASAP 2020 instrument after degassing the samples at 200°C for 4 h), electrochemical charge discharge analysis (Maccor cycle life tester, under the potential window 3.0–0.5 V).

Electrochemical characterization

The pristine and C@$Li_4Ti_5O_{12}$ anode slurry was made by mixing 87.5% of the synthesized C@$Li_4Ti_5O_{12}$ (85% of pristine), 5% super-p carbon (7.5% for pristine) and 7.5% of PVDF binder in NMP dispersant. Negative electrodes were produced by coating the slurry on copper foil and dried at 120°C for 1 h initially and at 100°C for 4 h in vacuum oven. The resulting slurry-coated copper foil was roll-pressed and the electrode was reduced to the required dimensions with a punching machine. Preliminary cell tests were conducted on 2032 coin-type cells, which were fabricated in an argon-filled glove box using lithium metal as the counter electrode and a micro porous polyethylene separator. The electrolyte solution was 1 M $LiPF_6$ in 1:1 EC:DEC.

Results and discussion

The schematic representation of the synthesis procedure is shown in Fig. 1a. The conductivity of the pristine $Li_4Ti_5O_{12}$ is very low (10^{-13} S/cm) owing to the existence of Ti in its tetravalent state, which limits its utilization in high-rate LIBs applications (Chen et al. 2001). Accordingly, carbon coating has been pursued as a strategy to alleviate the conductivity-related issues. Hence, in the current synthesis procedure, nanostructured mesoporous TiO_2 spheres with a surface area of 116.49 m^2/g were soaked with pitch, as a carbon precursor, and lithium carbonate in NMP solvent. As each TiO_2 sphere is assembled from a huge number of fine primary nanoparticles (10–20 nm) with high porosity, the pitch dissolved in NMP can easily creep into the TiO_2 spheres thereby ensuring complete coating of the primary particles.

Figure 1b shows the XRD patterns of typical materials synthesized using the above procedure at each step of the synthesis. The starting precursor is indexed to anatase TiO_2 with a tetragonal lattice structure (JCPDS card no. 21-1272). The nanosized pristine and carbon-coated $Li_4Ti_5O_{12}$ patterns can be assigned to the cubic spinel lattice structure (JCPDS file no. 49-0207). It is noteworthy that the XRD pattern of the

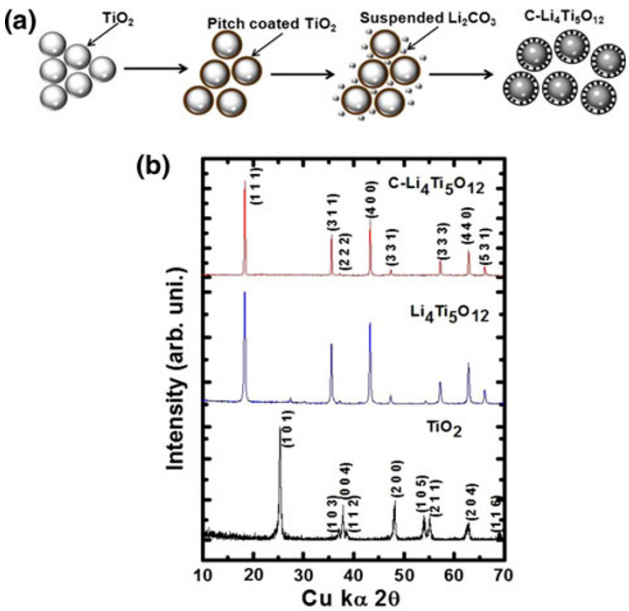

Fig. 1 Schematic representation of the synthesis procedure involved (**a**) and XRD pattern of the compounds synthesized (**b**)

$C@Li_4Ti_5O_{12}$ material is silent in the scattering vector range associated with carbon. This finding implies that the carbon is presented in disordered/amorphous form in the coating (Jayaprakash 2007). The mean crystallite size calculated from the (111) peak using Scherrer's formula is found to be about 25 nm for the $C@Li_4Ti_5O_{12}$, 52 nm for the pristine $Li_4Ti_5O_{12}$ and 15 nm for the TiO_2 precursor [from (101) peak]. It is noticeable from the calculated crystallite size values that there is a considerable increase in the average value after calcination at 900°C. The influence of high temperature calcination on crystallite size is noticeably less for the $C@Li_4Ti_5O_{12}$ particles, presumably reflecting the presence of a thin buffering layer of carbon. The amount of carbon present in the $C@Li_4Ti_5O_{12}$ sample has been determined by thermo gravimetric analysis to be $\sim$20 % (shown as inset in Fig. 4d).

The pore size distributions calculated by the Barrett–Joyner–Halenda method (Fig. 2a–d) for all materials studied confirm the presence of well-developed mesoporosity with very narrow pore-size distribution centered at 4, 6.5 and 4.7 nm for TiO_2, pristine $Li_4Ti_5O_{12}$ and $C@Li_4Ti_5O_{12}$ materials, respectively. The BET surface area values calculated are 29.9 and 49.7 m^2/g for pristine $Li_4Ti_5O_{12}$ and $C@Li_4Ti_5O_{12}$, respectively. As expected, the high temperature calcination step has reduced the surface area and porosity of both materials, considerably. This observation is in accordance with the average crystallite sizes calculated from the above XRD analysis.

The morphology of the synthesized materials was further examined by TEM measurements (Fig. 3a–d). It can be seen that the spheres are relatively uniform with diameters in the range of 300–500 nm. Furthermore, it is interesting to note the manner in which carbon has been coated to the $Li_4Ti_5O_{12}$ particles; it is apparent that carbon has been coated to the spherical core $Li_4Ti_5O_{12}$ particles uniformly, typically by generating a void space separating the core and the carbon coating (Fig. 3c). However, upon magnifying the TEM image to a higher resolution (Fig. 3d), it can be seen that the space in between is not completely void, but rather is packed with an ultra-thin filmy layer of amorphous carbon connecting the core and the outer carbon coating. It is expected that such a filmy layer of carbon will facilitate easy diffusion of Li^+ ions into the core $Li_4Ti_5O_{12}$ particle, in contrast to a bulky carbon deposit, during the electrochemical charge–discharge processes. Figure 3d represents an EDAX spectrum from the outer filmy layer, which confirms the existence of carbon alone as a spongy deposit on the particle exterior.

The electrochemical charge–discharge behavior of the nanostructured pristine and $C@Li_4Ti_5O_{12}$ materials was investigated using coin-type cells (2,032) comprised of the synthesized materials as the working electrode against

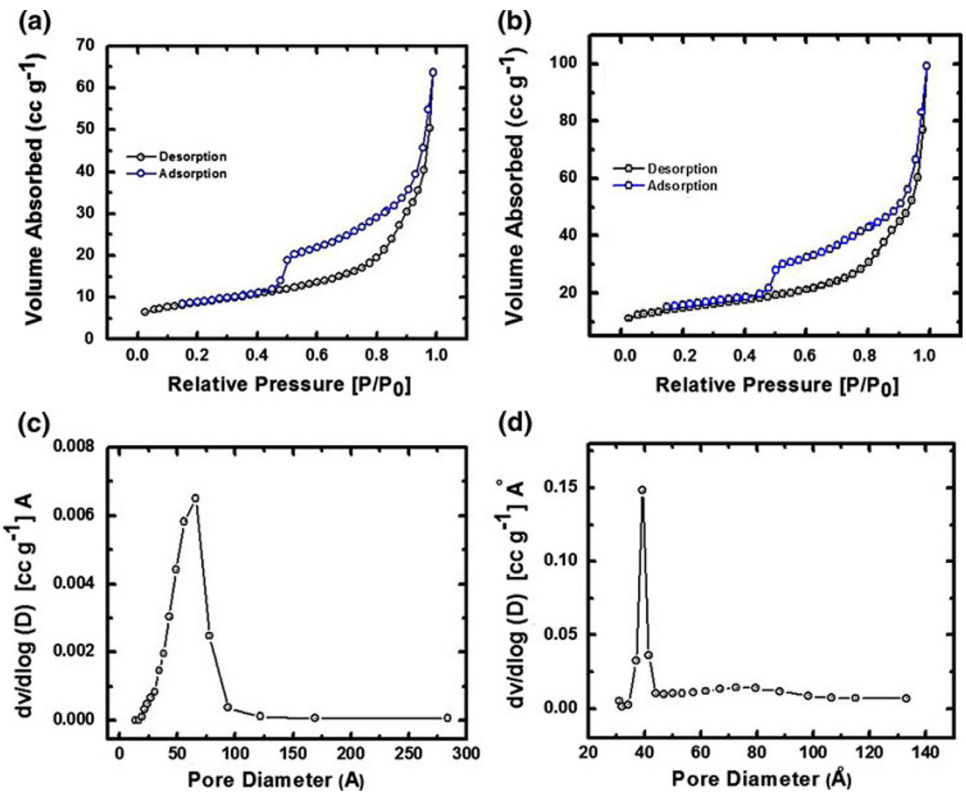

Fig. 2 BET surface area analysis of pristine (**a**) and $C@Li_4Ti_5O_{12}$ (**b**). Nitrogen adsorption–desorption isotherm of pristine (**c**) and $C@Li_4Ti_5O_{12}$ (**d**)

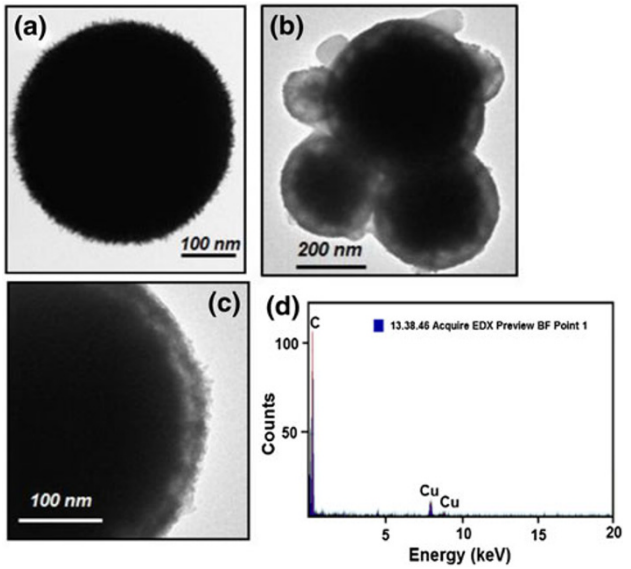

Fig. 3 TEM images of **a** TiO_2 and **b**, **c** C@$Li_4Ti_5O_{12}$ samples. **d** EDAX spectrum of the spongy outer later showing the presence of carbon alone

lithium metal counter electrode. The cells were discharged and charged at a 0.1C-rate for the first ten cycles and at a predetermined higher C-rate for the subsequent cycles under the voltage window of 3.0–1.0 V. The typical voltage versus capacity plots for the nanostructured pristine $Li_4Ti_5O_{12}$ and C@$Li_4Ti_5O_{12}$ materials are compared in Fig. 4a–c, wherein very flat Li^+ ion insertion and deinsertion plateaus around 1.54 and 1.57 V respectively are observed. Interestingly, despite its significant content of inactive carbon, the nanostructured C@$Li_4Ti_5O_{12}$ material delivers a higher initial discharge capacity of 166 mAh/g than pristine $Li_4Ti_5O_{12}$ (148 mAh/g) even at the relatively low rate of 0.1C. We suspect that this behavior stems from the smaller crystallite size and higher surface area of the nanostructured C@$Li_4Ti_5O_{12}$ active material in the anode. More significantly, after 120 cycles at a 1C-rate, the C@$Li_4Ti_5O_{12}$ material manifests a remarkably reversible capacity of 156 mAh/g, compared to only 76 mAh/g for pristine $Li_4Ti_5O_{12}$; underscoring the profound benefit of the carbon coating.

Figure 4c and d show the rate capability behavior of our pristine and C@$Li_4Ti_5O_{12}$ materials, wherein the cells were charge and discharged at the same C-rates, up to maximum of 7C, set by the current input restriction on the measurement device used for the charge–discharge cycling. As expected, the C@$Li_4Ti_5O_{12}$ exhibits superior rate capability behavior compared to the pristine $Li_4Ti_5O_{12}$. Specifically, the nanostructured C@$Li_4Ti_5O_{12}$ delivers a specific charge capacity of 161 mAh/gat a 0.1 C-rate which upon increasing the current rate has reduced to 155, 147, 141, 132 mAh/g, respectively with respect to 1, 2, 3, 5 and 7 C-rates. On the other hand, the pristine $Li_4Ti_5O_{12}$ though

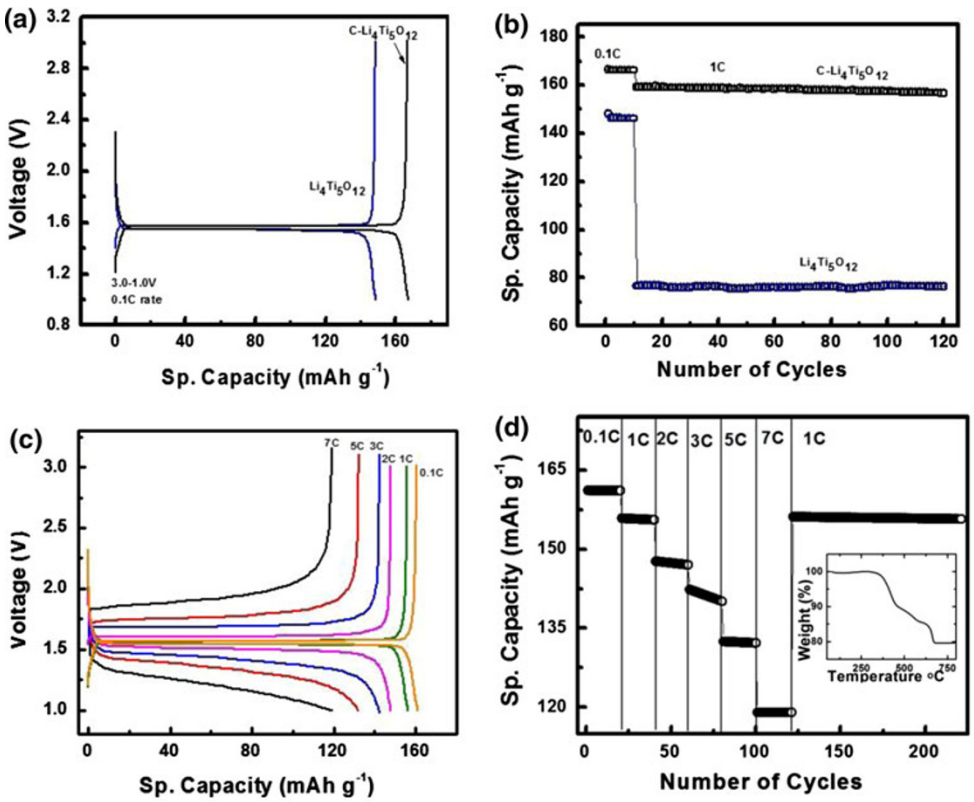

Fig. 4 Voltage versus capacity (**a**) and cycle life behavior (**b**) of pristine and C@$Li_4Ti_5O_{12}$ samples. **c**, **d** Rate capability behavior of the C@$Li_4Ti_5O_{12}$. *Inset* to (**d**) depicts the TGA analysis showing the presence of 20% of carbon in the C@$Li_4Ti_5O_{12}$ composite

also delivering stable capacity behavior, exhibits very low capacities at extended C-rates. Lastly, these results also show that the material is unchanged after cycling for extended periods at multiple high rates—a capacity of 155 mAh/g is regained when the rate is lowered to 1C after lithium extraction at various C-rates (Fig. 4d).

Conclusions

In conclusion, a simple scalable chemistry has been developed to synthesize nanostructured, mesoporous carbon-coated $Li_4Ti_5O_{12}$ with high surface area. Carbon is derived by carbonizing low-cost petroleum pitch at high temperature. When used as anode in LIB, the as-synthesized C@$Li_4Ti_5O_{12}$ exhibits significantly enhanced electrochemical performance, particularly at high current densities. The amount of carbon required for a better performing C@$Li_4Ti_5O_{12}$ was found to be $\sim$20 wt%. The combination of fast electrolyte and ion transport made possible in the inherently zero-strain material, $Li_4Ti_5O_{12}$, is thought to be responsible for our observations. We anticipate that the combination of scalable synthesis, inherently safer operation, and exceptional high-rate performance will make anodes based on mesoporous C@$Li_4Ti_5O_{12}$ attractive for practical high power LIBs.

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